QUANTUM CHEMISTRY AND EXCITED STATES:
FIRST INVESTIGATIONS ON PYRENE-LIKE MOLECULES.

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Introduction

Aromatic molecules are now recognized as an important component of the interstellar medium. Although no direct and definite observation has been reported, they are likely candidates for the carriers of the so-called Unidentified Infrared Bands (UIR) (Allamandola et al., 1985; Léger and Puget, 1984). Both theoretical calculations (Pauzat et al., 1992; DeFrees et al., 1993; Pauzat et al., 1994) and experimental results (Szczepanski et al., 1992; Hudgins et al., 1994) support such an assumption provided that the species are either ionized or dehydrogenated. Lot of works, both on the theoretical and experimental sides have been done in the last years to achieve these results.

However, the problem of the identification of the carriers of the famous Diffuse Interstellar Bands (DIBs), which can be considered as the counterpart of the UIR emission in the visible region remains wide-open since more than 70 years. Cations of Polycyclic Aromatic Hydrocarbons (PAHs) have been known for a long time to strongly absorb in the visible (Shida and Iwata, 1973) and have been proposed as attractive candidates (Van der Zwet and Allamandola, 1985; Léger and d'Hendecourt, 1985; Crawford et al., 1985). But despite many experimental studies by several groups, no one-to-one unquestionable attribution has been made for the DIBs in the PAH hypothesis although presumptions are increasing (Salama and Allamandola, 1991, 1992ab, 1993; d'Hendecourt and Léger, 1993, 1994) .

It has recently been proposed that some pyrene-like molecules could account for the strongest 4430 Å DIB (Salama and Allamandola, 1992b, 1993). This assumption is based on the fact that side-substituents could induce shifts in the transition energies of the pyrene cation so that a good match with this DIB could be reached. Parallel and independently, experimental works have been undertaken on such species by the IAS group who has recorded the visible spectra of the products obtained by ionization of 1-methyl-pyrene. An excellent agreement with (at least) 4 DIBs has been observed (d'Hendecourt and Léger 1993, 1994), but some doubts remain regarding the exact structure of the corresponding carrier: 1-methyl-pyrene cation, 1-methylene-pyrene or, why not, dehydrogenated or hydrogenated species.

The side-substituent effect approach seems to be a very attractive and promising approach but will lead to new experimental problems due to the difficulties in obtaining unambiguously defined compounds following ionization. Furthermore, it must be kept in mind that the shifts induced by substitution will not depend only on the nature of the substituent but also on its position on the aromatic cycle. There are then so many pos-

sibilities in the choice of the species to investigate and so few unquestionable arguments to rule out possible carriers that it represents a formidable experimental task.

Quantum chemistry calculations are thus an attractive alternative to help in the choice of possible candidates. A few years ago, such calculations have been undertaken in our group on the electronic absorption spectra of neutral and ionized PAHs (Parisel et al., 1992; Parisel and Ellinger, 1993), at a time where no experimental spectra were avalaible for a direct comparison with the astrophysical observations. This work gave an excellent agreement with the now avalaible rare-gas matrix spectra (Szczepanski et al., 1993; Vala et al., 1994).

In this paper we will illustrate the possibilities of such calculations on the three methyl-pyrene cation isomers.

Methodology

The method we use has been described elsewhere (Parisel et al., 1992) and only a short description will be given here. Due to the size of the molecule under study, an ab initio calculation of both the ground and the excited states is unrealistic. We will then turn to a π-electron semi-empirical approach known as the PPP method (Pariser and Parr, 1953; Pople, 1953; Berthier et al., 1953). It can be seen, roughly speaking, as an extension of the famous Hückel theory to a quantitative self-consistent-field calculation by the inclusion of the most important bielectronic integrals. The description of the excited states is reached by the use of a multistate multireference method that couples perturbation and variation. The so-called CIPSI method (Huron et al., 1973) has the advantage of giving a well-balanced description of the excited states, if properly used. The effective PPP hamiltonian we used was optimized at the PPP+CIPSI level of theory on the pyrene cation so that the first allowed calculated transition matches the first intense experimental transition. The final spectrum obtained with this optimized hamiltonian was found to be in excellent agreement with both the recent absorption spectra of the pyrene cation and the photoelectron spectrum of the neutral pyrene (Salama et al., 1993; Vala et al., 1994).

The side-methyl group was described as a fragment being made up of a carbon atom coupled to a pseudo 'H_3' atom, as proposed by Lévy and Berthier (1966) who have determined the corresponding atomic parameters by optimization on the absorption spectrum of the toluene molecule.

In all calculations, standard bond lengths and bond angles were used, assuming a C_s

transition	pyr$^+$		1-Me-pyr$^+$		2-Me-pyr$^+$		4-Me-pyr$^+$	
	E	f	E	f	E	f	E	f
1	6857	forb.	9116	0.016	3277	0.001	7697	0.016
2	12647	0.033	12617	0.066	12235	0.016	10319	0.063
3	13969	0.021	14554	0.033	13611	0.021	14556	0.006
4	19575	0.054	18682	0.133	14164	0.036	18610	0.034
5	23858	0.362	21894	0.390	21722	0.001	21730	0.030
6	29318	0.109	23948	0.011	22754	0.001	23203	0.306
7			26089	0.000	23543	0.374	23838	0.000
8					25562	0.133	27127	0.007

Table 1. Transition energies (cm^{-1}) and oscillator strengths for the pyrene cation and its methyl derivatives.

geometry for the 1- and 4-methyl-pyrene skeletons, but a C_{2v} structure for the 2-methyl-pyrene cation. All calculated transitions are vertical, and no vibronic interaction has been taken into account in this treatment.

Results and discussion

The calculated transition energies up to 26000 cm^{-1} and the corresponding oscillator strengths for the 3 possible isomers of the methyl-pyrene cation are reported in table 1 together with those obtained previously for the unsubstituted pyrene cation (Vala et al., 1994).

First, it can be seen that the substitution leads to the emergence of a weak and low-energy absorption band. This new band corresponds to the first transition which is forbidden in the D_{2h} pyrene cation and which becomes allowed due to the lowering of the symmetry going from a D_{2h} to C_{2v} or C_s structures.

Second, it should be pointed out that the spectra of the substituted species roughly look like the spectrum of the pyrene cation. Such a behavior with substitution has to be expected provided the substituent does not induce new conjugation effects with the rings, which is the case for alkyl ones.

However, if we now compare the spectra in more details, important changes have to be noticed. If 1- and 4-methyl-pyrene cations give close spectra, 2- and 4-methyl-pyrene cations lack a strong transition in the 21000 cm^{-1} region. Furthermore the 2-methyl

isomer exhibits a strong absorption at 25562 cm^{-1} which is not observed in the other two members of the series.

Let us now turn to a comparison with the strongest 4430 Å DIB. It is seen that in the 3 possible isomers, the strong absorption band of the pyrene cation at 23858 cm^{-1} is shifted to a lower energy and draws nearer to 22573 cm^{-1} which corresponds to the 4430 Å DIB. 4-methyl-pyrene cation gives the best match, only 630 cm^{-1} far from that DIB. A comparable discrepancy is observed for the 1-methyl isomer, but the difference obtained for 2-methyl-pyrene cation is larger (970 cm^{-1}) and the corresponding oscillator strength too small to account for this DIB.

Let us consider another strong DIB, namely the 7564 Å one (13221 cm^{-1}): it is seen that 1-methyl-pyrene cation provides an absorption at 12617 cm^{-1} while the other isomers either do not exhibit any absorption in this region or have only a very weak band around this position.

If we now take a look at a third DIB at 5780 Å (17300 cm^{-1}), 2-methyl-pyrene cation has to be ruled out since its nearest transition to that DIB is more than 3100 cm^{-1} away from it: in fact, its spectrum presents a hole in that region. The situation is less clear for the two remaining isomers with shifts of about 1300 cm^{-1} relative to this DIB. However the transition carried by the 4-methyl-pyrene cation has a very low oscillator strength and thus is a poor candidate.

We also note that the strong 1-methyl-pyrene cation transition at 18682 cm^{-1} falls close to the strong 5362 Å (18650 cm^{-1} DIB, 4-methyl-pyrene having only a weak transition in that region.

Finally, we point out that the first transition of the 1-methyl isomer at 9116 cm^{-1} is only 600 cm^{-1} far away from another strong DIB at 11797 Å.

The previous discussion shows that among the three isomers of the methyl-pyrene cation, the 2- and 4-methyl species are unlikely to account for more than one strong DIB, contrary to the 1-methyl compound.

Conclusion

We expect our calculations to be accurate within 10 %: it follows then that we cannot propose unquestionable one-to-one attribution due to the density of the DIBs. Nevertheless, we have shown that if one is interested in the experimental study of methyl-pyrene cations, for example, then, the most promising candidate is the 1-methyl isomer: this isomer has been investigated by d'Hendecourt and Léger (1993, 1994) and their spec-

trum shows very striking features in very good agreement with both our calculations and a few DIBs . However, 1-methyl-pyrene cation is not the only product susceptible of being formed in this experiment, and further investigations are in progress to give a complete interpretation of the results.

This preliminary report on pyrene-like molecules illustrates the role that theoretical calculations can play in both the design and the interpretation of experiments.

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